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# Decrease in surface ozone concentrations at Mediterranean remote sites and increase in the cities

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## HIGHLIGHTS

- We calculate annual trends for ozone and associated statistics.
- We discuss of spatial distribution of levels and changes in ozone concentrations.
- We use an innovative method by co-kriging to map results.
- We discuss of possible explanations of observed trends.
- We discuss of the convergence of ozone pollution at remote and urban sites all around the Mediterranean Europe.

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## ABSTRACT

Analyzing hourly ozone data from 214 European background sites over the time period 2000–2010, we demonstrated for the first time that the ozone control measures are effective at rural sites, while ozone concentrations are still increasing in the cities. The Western European Mediterranean basin is expected to be more strongly affected by climate change, including ozone pollution, than most of the other regions of the world. At 58% of the rural sites significant decreases were found resulting in an average − 0.43% per year while an increase was recorded in urban and suburban stations (+0.64% $year^{-1}$ and +0.46% $year^{-1}$, respectively). At cities ozone average levels increased, but the peak ozone concentrations decreased. In all station types, a significant reduction in the amplitude of peak ozone concentrations was found at more than 75% of stations (98th percentile, −0.77% $year^{-1}$; hourly peak, −1.14% $year^{-1}$ and daily average peak, −0.76% $year^{-1}$). The peak reduction may largely be attributed to the reduction in $NO_x$ and VOC emissions within the European Union which started in the early 1990s. The results suggested a convergence of ozone pollution at remote and urban sites all around the Western European Mediterranean basin.



## 1. Introduction

Ground-level ozone ($O_3$) is an important atmospheric pollutant and climate forcer. The majority of surface ozone formation occurs when nitrogen oxides ($NO_x$), carbon monoxide (CO) and volatile organic compounds (VOCs) react in the atmosphere in the presence of sunlight. Ozone, the third important greenhouse gas in terms of radiative forcing (Ramaswamy et al., 2001), is an important air quality issue. The lifetime of tropospheric $O_3$ varies from one or a few days in the boundary layer to a few tens of days or even a few months in the free troposphere which enables transport from regional to hemispheric scale and hence proportionally greater influence on climate than $O_3$ near the surface. The localized sources of $O_3$ precursors and generally short lifetime of surface $O_3$ make its distribution spatially non-uniform and time-variant (Schwartz, 1989; Zanis et al., 2007). The negative effects of the surface $O_3$ on human health, crops, forests and materials have been widely discussed since the 1950s (Richards et al., 1958; Mckee, 1994; Krupa et al., 2001; Mills and Harmens, 2011; Dalstein and Vas, 2005,

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2008; Contran and Paoletti, 2007; Paoletti, 2006, 2009; Paoletti and Manning, 2007; Screpanti and De Marco, 2009; De Marco, 2009; Sicard et al., 2011a, 2012).

In view of the harmful effects of photochemical pollution in the lower levels of the atmosphere, the European Council adopted a first Directive on air pollution by ozone in 1992 (92/72/EEC). It established procedures for harmonized monitoring of surface ozone concentrations. An important objective of many environmental monitoring programs is to detect changes or trends in pollution levels over time. More than 20 years later, it is now of interest to verify the effectiveness of the control measures, in lowering both the emission of ozone precursors and the ambient ozone levels.

Following Kourtidis et al. (1997), "natural background" means ozone generated chemically in the troposphere from non-anthropogenic emissions (biogenic and geogenic such as trees, agricultural crops, lightning) plus ozone transported from the stratosphere. Ozone trends are caused by a background hemispheric trend and regional changes (emissions, meteorology…). The establishment of annual ozone trends is important for quantifying the impact of changing precursor emissions and also from the perspective of local and regional air quality control. Rural areas are influenced by the large-scale dispersal of precursors produced at urban and regional scales, and, are the most representative of background pollution at global scale and allow an assessment of the impact on ecosystems (De Leeuw, 2000; Sicard et al., 2009).

The annual cycle and trends of surface ozone at northern and western parts of Europe has been widely studied at rural, suburban and urban sites (Logan et al., 1999; Monks et al., 2003; Vingarzan, 2004; Solberg et al., 2005; Lelieved et al., 2004; Jonson et al., 2006; Derwent et al., 2007; Wilson et al., 2012; Parrish et al., 2012). Since 1950s surface ozone concentrations have increased at background rural sites of the northern mid-latitudes by 1–2% year$^{-1}$ (Logan et al., 1999). In Northern Hemisphere, the ozone levels increased over the Northern Atlantic (Lelieved et al., 2004) producing persistent levels of ozone at rural and urban areas of the European Atlantic Coast (Derwent et al., 2007). Similar trends can be observed at the United States Pacific Coast (Jaffe and Ray, 2007). Significant positive trends in ozone mean concentrations during the 1990s were observed at Northern European rural sites (Vingarzan, 2004). Most sites showed substantial downward trends of high ozone (98 or 95th percentiles) over the past 15 years (Wilson et al., 2012). As an example peak ozone concentrations have decreased by 30% in the United Kingdom (Coyle et al., 2003) and the 99th percentile dropped in Germany between 1990 and 2000 (Beilke and Wilson, 2000).

The Mediterranean basin has many morphologic, geographical and societal characteristics, which make its climate scientifically interesting. Climate change is expected to be more pronounced in the Mediterranean Basin than in most other regions of the world (IPCC, 2001). Whereas temperatures should increase on average by 1.4–5.8 °C worldwide, the difference should be at least 3 °C in the Mediterranean Basin and the Mediterranean Basin will be one of the areas subject to the most drastic reductions in precipitation (IPCC, 2001). Temperatures are expected to continue to increase in the coming decades, with considerable effects on human society and the environment (EEA, 2004). Formation of ozone is dependent on temperature and is higher during the plant growing period (ICP, 2007). A substantial increase in water shortage is expected, due in large part to the increase of temperatures rather than to the decrease in rainfall; therefore, the risk of drought in summer will increase around southern Europe. As $O_3$ exposure is expected to unbalance water control of vegetation (Paoletti and Grulke, 2010), such climate changes stress once more the importance of a proper assessment of $O_3$ risk to vegetation, in particular in Mediterranean climate. Overviews of the consequences of climate changes and ozone pollution for trees in the Mediterranean basin are provided by Bakkenes et al. (2002), Petit et al. (2005) and Paoletti (2006).

The European region at highest $O_3$ risk is the Mediterranean area because of several main reasons. Ozone formation occurs at high temperature in presence of solar radiation, which is elevated in Mediterranean-type ecosystems (Alonso et al., 2001). In summer, anti-cyclonic subsidence, low winds, and strong insolation favor massive photochemical production of $O_3$, and inhibit recirculation within air masses (Millan et al., 2000). Some areas are subjected to high road traffic and industrial emissions, e.g. the megalopolis/metropolis effect of Marseille in France and Genoa and Milan in Italy (Sicard et al., 2011a).

Surprisingly, however, a comprehensive analysis of surface ozone data and ozone precursor's trends in the Mediterranean Europe has not been carried out. This study aims to characterize and quantify surface ozone concentrations and trends in "67" rural, "74" suburban and "73" urban background sites around the Western European Mediterranean basin (East Spain, Malta, South France and Italy) over the time period 2000–2010, and assess the impact of the changing precursor emission on the time trends.

## 2. Materials and methods

### 2.1. Data selection and methodology

Ozone data were kindly provided by the Air quality database AirBase of the European Environment Agency (EEA). Hourly ozone concentrations were obtained for background stations (rural, suburban and urban) over the period 2000–2010 over a strip of land of 200 km along the European coast of the Mediterranean Sea. We selected the stations with more than 75% of validated hourly data per year. The following annual statistics were calculated: 24-h mean concentration, median, 98th percentile, average daily maximum and hourly peak maximum. Over the time period 2000–2010, 214 stations were selected in Spain, France, Italy and Malta. Insufficient station distribution did not allow us to include the Eastern Mediterranean part of Europe into this analysis (data not shown).

Ozone monitoring stations are called urban, when they are located in a city. Residential areas outside a main city represent the suburban zone of a monitoring station. When a station is located outside a city, far from city sources of air pollution, the type of zone is called rural. When the pollution level is not significantly affected by any single source, but by the integrated contribution from all sources upwind of the station, the station is located on a background area (Snel et al., 2004). In order to explore the factors driving the observed surface ozone trends, emission of ozone precursors (namely, $NO + NO_2 = NO_x$, CO and VOC) were examined during both the period 2000–2010 and over a 20-years period (1990–2010). The European emissions are provided by the European Monitoring and Evaluation Programme (EMEP).

### 2.2. Estimation of annual trends

The Mann–Kendall test is a non-parametric statistical test to detect the presence of a monotonic increasing or decreasing trend within a time series. Data were checked for normal distributions with the Kolmogorov–Smirnov D test. Statistical tests for monotonic trend in ozone time series are commonly confounded by some of the following problems: non-normal data, missing values, seasonality, censoring (detection limits) and serial dependence. Because the test is based on ranks, the advantage of the non-parametric tests over the parametric tests is that they are robust and more suitable for non-normally distributed data with missing and extreme values, frequently encountered in environmental time